Competing interactions in arrested states of colloidal clays

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Using experiments, theory and simulations, we show that the arrested state observed in a colloidal clay at intermediate concentrations is stabilized by the screened Coulomb repulsion (Wigner glass). Dilution experiments allow us to distinguish this high-concentration disconnected state, which melts upon addition of water, from a low-concentration gel state, which does not melt. Theoretical modelling and simulations reproduce the measured Small Angle X-Ray Scattering static structure factors and confirm the long-range electrostatic nature of the arrested structure. These findings are attributed to the different timescales controlling the competing attractive and repulsive interactions.

Dynamical arrest in soft colloidal systems has recently become the subject of an intense research activity. The fine tuning of control parameters opens the possibility to tailor the macroscopic properties of the resulting non-ergodic states. Several mechanisms of dynamical arrest have been identified. Building on the knowledge on the hard spheres glass [1], it has become recently clear that when both attractive and repulsive terms are present in the interaction potential, a re-entrant liquid-glass line, surrounded by two distinct glasses, has been predicted and experimentally observed in short-ranged attractive colloids at high concentrations [2]. A rich phenomenology also takes place at low concentrations: here gelation occurs, which may result from different routes [3]. Interesting scenarios arise when, in addition to a short-ranged attraction, particles have a residual electrostatic charge which builds up a long-range repulsion in the effective potential. In this case, particles can form equilibrium clusters [4], which provide the building blocks of arrest [5]. Recent works have shown that both Wigner glasses [6], intended as arrested states formed by disconnected particles or clusters and stabilized by the electrostatic repulsion, and equilibrium gels, which occur at larger packing fractions when the clusters branch into a percolating network, can form under these conditions [7, 8].

To investigate the formation of multiple arrested states, colloidal clays [9, 10] have emerged as suitable candidates. The anisotropy of the particles, combined with the presence of attractive and repulsive terms in the interactions, makes the phase diagram of such colloidal systems very complex. Among these, Laponite suspensions have been widely studied not only for their appealing industrial applications [11] but also for their interesting experimental/theoretical properties [12–20]. In particular, Laponite displays a non-trivial aging dynamics [15] and (at least) two final arrested states, which are obtained by a simple increase of Laponite volume fraction from low ($C_w < 2.0\%$) to moderate ($C_w \geq 2.0\%$) values, at fixed salt concentration $C_s = 10^{-4}M$ [15, 17].

More recently, the static properties of these two states have been investigated in detail [18], showing that they are also characterized by both the very different aging behaviors and the shape of the static structure factor $S(Q)$. While the low C_w state shows typical inhomogeneities, the high C_w state is homogenous, allowing for the identification of these two arrested states respectively as gel and glass.

In this Letter, through the combination of experiments, numerical and theoretical approaches, we demonstrate that the non-ergodic state observed in Laponite samples in salt free water at sufficiently large concentrations ($C_w \geq 2.0\%$) is a Wigner glass. By performing a simple but impressive dilution experiment, we are able to distinguish whether attractive or repulsive interactions are dominant in the formation (and stability) of the arrested structure for both low and high concentration arrested samples. Moreover, we compare the $S(Q)$ determined by Small Angle X-rays Scattering (SAXS) with theoretical and numerical ones in the high concentration window, providing an estimate for the effective interactions between Laponite platelets. These results provide clearcut evidence that the resulting large concentration arrested state (which is still found at very low packing fraction) can be attributed to the residual electrostatic repulsion (Wigner glass) [6]. Thereby Laponite offers the unique example of a system which, not only displays two distinct non-ergodic states differing only in colloidal concentration, but also shows a counter-intuitive scenario which involves gel-like structures at lower concentrations and a (truly) disconnected glass at larger ones. Hence, the increase of concentration, which normally favours percolation and branching, here has the opposite effect. We attribute this novel behavior to the interplay of different time-scales in the involved attractive and repulsive interactions, a feature that may be found in other complex colloidal systems.

To investigate the glassy state formed by Laponite at high clay concentration ($C_w \geq 2.0\%$) [15, 17, 18], we
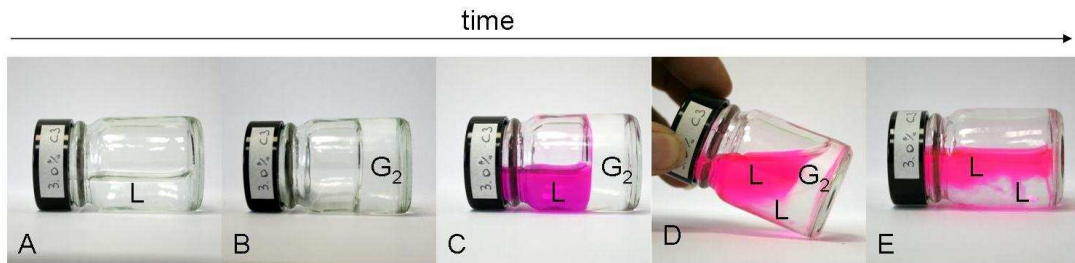
FIG. 1: Evolution of a high concentration sample at $C_w = 3.0\%$ with time. The initially liquid (**L**) sample (A) ages with time reaching, after 50 h, a final arrested glassy state (**G$_2$**)(B). At this time a colored solution (in a liquid (**L**) state) is added to the arrested sample (C) that starts to fluidize at the interface (D)- 70 h. Finally the whole sample is liquid again (E) - 120 h.

use a combination of different approaches. Firstly, we perform a dilution experiment (adding water to the arrested state) that provides a direct criterion to establish the dominant interactions controlling the formation and stability of the arrested state [3]. If this were due to attractive interactions, the presence of additional water should not affect the final state, because Laponite bonds (of strong electrostatic nature) can not be broken by the mediation of water. On the other hand, if repulsive interactions are determining the formation of the non-ergodic state, the increase of free volume allows a rearrangement of the Laponite platelets on average to a larger distance. If such distance is larger than the characteristic repulsive length (namely the electrostatic Debye length) the glass will be destabilized up to melting to a liquid state.

To obtain reliable and reproducible results [21] Laponite RD dispersions are prepared using the same protocol described in [18]. The starting waiting time ($t_w = 0$) is the time at which the suspension is filtered. For the dilution experiment a sample at high clay concentration, $C_w = 3.0\%$, is filtered and sealed in small glass bottles. The photographic sequence of this experiment is shown in Fig.1. The initially liquid (**L**)((A) panel) sample ages with time ≈ 50 h [15] until reaching a final arrested state, as it can be seen in panel (B) where the sample shows its solid like nature (**G$_2$**). At this point a solution of colored water (of the same volume as that of the Laponite solution) is added to the arrested (colorless) sample. The colorant used, Rhodamine B at a concentration $10^{-3} M$, does not play any role in the process, as shown below, and is used to better distinguish (C panel) the arrested sample (**G$_2$**) from the liquid solution (**L**). After the addition of water, the arrested sample starts to fluidize at the interface with the liquid solution (D panel - $t_w = 70$ h). This process evolves with time until, after 120 h, the whole sample is back into a liquid state (E panel). This result strongly speaks in favor of the repulsive nature of the $C_w = 3.0\%$ arrested state. The experiment is repeated in absence of Rhodamine and shows that the addition of the dye does not affect the results. We have monitored that the pH of the solution remains constant throughout the dilution experiment.

We now turn to elucidate the effective interactions between Laponite platelets, by comparing the evolution of the experimental static structure factor $S^M(Q)$, obtained from SAXS measurements performed at the High Brilliance beam line (ID2) [22] at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, as described in [18], with that predicted theoretically $S^{th}(Q)$, assuming several effective interaction potentials [23].

In Fig. 2 the comparison between $S^M(Q)$ (symbols) and optimal $S^{th}(Q)$ (lines), for fixed $t_w \simeq 50$ h in the concentration window $2.0\% \leq C_w \leq 3.0\%$, is shown. As it is evident from Fig. 2, as concentration is decreased from $C_w = 3.0\%$ to $C_w = 2.0\%$ the low Q signal is slightly increased and the main peak is slightly shifted towards lower Q values. The position of the main peak is around $Q \sim 0.17$ nm^{-1}, corresponding to a length ≈ 37 nm, a value clearly larger than the platelet diameter $d = 25$ nm, pointing to a non-connected final structure. Moreover, no evidence of a peak at contact distance is found.

The theoretical $S^{th}(Q)$ is calculated by solving numerically the Ornstein-Zernike equation with an appropriate closure relation [24] or by direct simulation of the effective potential, without a significant change in the description of the experimental data. For simplicity, we report Percus-Yevick results in the following. In this simplified treatment, we consider only the centers of mass of the scattering objects, supposedly single platelets, and treat them as (spherical) points, following previous work on different systems [7]. The main fit parameters involved in the description of the experimental data are the number density ρ of the scattering objects and the number of counter-ions N_{ci} that dissociate (on average) from each platelet when dissolved in water. Our study indicates that ρ cannot be the same as the number density of Laponite discs obtained from the nominal weight concentration $\rho_L = 2.4 \cdot 10^{22}/m^3$. Indeed, no simple interaction potential is able to reproduce the position of the main peak using ρ_L. Hence ρ must be smaller, due to the fact that platelets may be found within a distribution of clusters [25]. We find that the data can be fully described, in terms of peak position, peak height and compressibility, by a Yukawa potential, which accounts
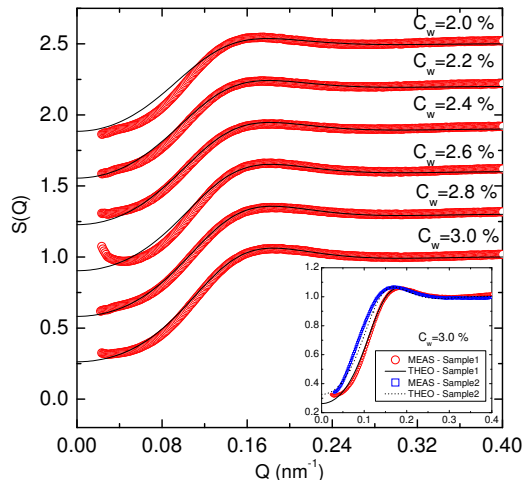
FIG. 2: Comparison between measured $S^M(Q)$ (symbols) and theoretical $S^{th}(Q)$ (lines) for several high concentration Laponite samples at $t_w \simeq 50$ h. For clarity, curves have been shifted along the vertical axis progressively by 0.3. Inset: Comparison between $S^M(Q)$ (symbols) and $S^{th}(Q)$ (lines) for two different samples with $C_w = 3.0\%$.
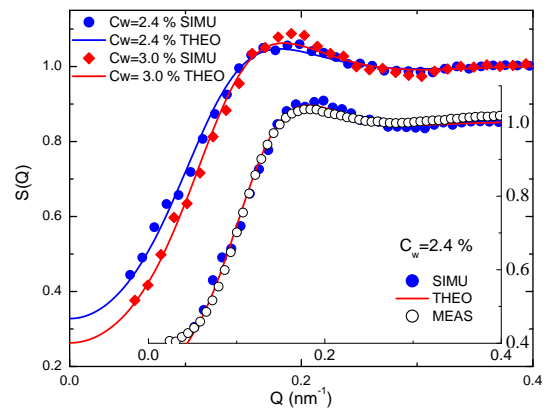

FIG. 3: Comparison between simulated (symbols) and theoretical (lines) S(Q) for $C_w = 2.4\%$ and 3.0% Laponite samples. Inset: Simulated (cross symbols), theoretical (line) and measured (open circles) $S(Q)$ for $C_w = 2.4\%$.

in an average way [7] for the screened electrostatic repulsion between Laponite platelets or clusters, in agreement with more sophisticated theoretical approaches [19]. We use a potential of the form $V_{eff} = A\xi e^{-r/\xi}/r$, where ξ is the Debye screening length and A provides a measure of the strength of the repulsion. The number density is fixed to $\rho \simeq 0.38\rho_L$, a relationship which is found to hold in the whole investigated concentration window. This suggests that Laponite may be dispersed in a distribution of very small aggregates, possibly due to particles that are not completely delaminated, compatibly with an AFM study performed under very dilute conditions [25]. The number of counterions in solution is optimized to $N_{ci} = 60$, a value well below the bare charge of a single platelet ($700 \quad e$), in good agreement both with previous simulations [19] and with conductivity measurements [17]. With this choice of parameters, the change in nominal concentration and its associated screening length ξ, varying between 8 and 10 nm, are able to reproduce $S^M(Q)$ in the full investigated window, as seen in Fig. 2. The repulsion strength $A\xi/k_BT$ is found to increase in the studied range of concentration by a factor of ≈ 2, compatibly with the behavior of other charged systems [26].

While the Yukawa potential correctly reproduces the experimental data, other possible candidates do not. The simple hard sphere model does not capture at all the softness of the interactions, failing to reproduce the low-Q regime also after one adjusts ρ. On the other hand, the addition of a short-range attraction to the electrostatic repulsion is (i) not sufficient to explain the low Q-position of the main peak; (ii) tends to induce an enhanced structuring at nearest-neighbour length. There-

fore, we conclude that no relevant attractive features are present in $S(Q)$ in this concentration window. Hence, the combination of the dilution experiment with the theoretical analysis allows to identify the observed arrested state as a Wigner glass stabilized by the residual electrostatic repulsions.

One further comment concerns the robustness and reproducibility of our findings for different samples. Although different measurements can bring small changes in $S^M(Q)$ due to differences in Laponite batches, to the filtration procedure or to real clay concentrations, we can fit equally well different samples with the same effective Yukawa potential upon variation of the fit parameters. This is shown in the inset of Fig. 2 where $S^M(Q)$ is reported for two different samples with $C_w = 3.0\%$, from different batches, measured in two different runs, in comparison with $S^{th}(Q)$. For the second batch, which has a higher polydispersity, we find $N_{ci} = 90$ and $\rho = 0.26\rho_L$.

The theoretical approach we have adopted so far treats only the correlations between the centers-of-mass of the scattering objects. Although such an approach was proven to be a good (although crude) approximation to describe the static correlations between equilibrium clusters of non-spherical shape [7], it is crucial to show that this treatment is valid also when we take into account explicitly the actual disc shape of clay particles. To this aim, we have performed MonteCarlo simulations of 200 discs at the same ρ as that extracted from the fits. We use the interaction model introduced in [27] where the total negative charge is uniformly distributed over the surface area, while rim charges are neglected. Each Laponite platelet is schematized as a rigid disk, composed by 19 sites disposed on a regular mesh. We simulate several repulsion parameters and find that the numerical $S^n(Q)$ is in good agreement with the experimental and theoretical ones when the total charge is fixed to 70 e and the screening length is 5 nm. Results are shown in Figure
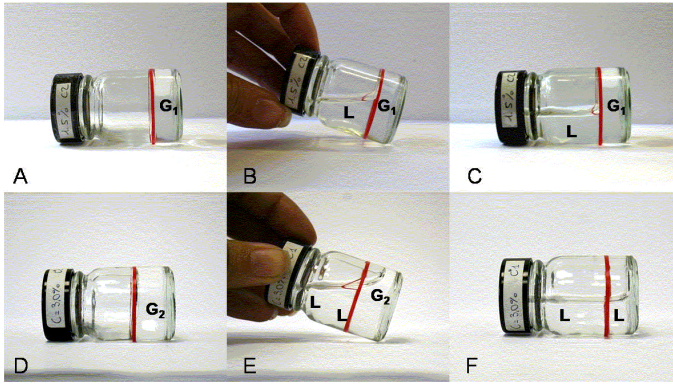
FIG. 4: Starting (A), intermediate (B) and final (C) states of a low concentration sample at $C_w = 1.5\%$: the initial gel state $\mathbf{G_1}$ is not macroscopically affected by the addition of water (C). Starting (D), intermediate (E) and final (F) states of a high concentration sample at $C_w = 3.0\%$: after the addition of water (**L**) the original glassy state $\mathbf{G_2}$ fluidizes (F).

3 for two samples with $C_w = 2.4\%$ and $C_w = 3.0\%$, in comparison with $S^{th}(Q)$. In the inset, simulated, theoretical and measured $S(Q)$ for sample $C_w = 2.4\%$ are compared. Hence, the favorable comparison of simplified theory and simulations with experimental measurements provides evidence that our effective approach is useful to describe disc-shaped objects in this regime.

So far we have reported evidence of the existence of a Wigner glass state in Laponite by the combination of experiments, theory and simulation for $2.0\% \leq C_w \leq 3.0\%$. At lower concentrations structural measurements have shown a marked growth of $S(Q)$ at low Q with waiting time, which was attributed to the presence of attractive interactions determining an arrested state of attractive (or gel) nature [18]. Already for the lowest concentration shown here ($C_w = 2.0\%$), the agreement between $S^M(Q)$ and $S^{th}(Q)$ is less good in the low Q range, as visible in Fig. 2. This might be an indication of the increasing role of attractive interactions upon lowering concentration. Hence, we perform the dilution experiment also for a low concentration sample expecting a different result with respect to the high concentration one.

In Fig. 4 the dilution experiment is shown for a low ($C_w = 1.5\%$) and a high ($C_w = 3.0\%$) concentration sample. The samples are left to age up to the final corresponding arrested states, respectively of gel ($\mathbf{G_1}$) and glass ($\mathbf{G_2}$) nature for low and high concentrations [18]. While the sample at $C_w = 3.0\%$ arrests within 50 h, the one for $C_w = 1.5\%$ takes several weeks [15, 17]. After arrest takes place deionized water (**L**) is added and panels (A) and (D) show the identical situation for the two cases. However the evolution of the two samples soon becomes dramatically different. The arrested state of the high concentration sample ($\mathbf{G_2}$) starts to fluidify ((E) panel) up to reach a final liquid state ((F) panel). On the contrary, the low concentration sample does not

liquify and does not show any macroscopic changes of its solid like state, even after waiting additional weeks, i.e. the same timescale of the arrest process. In this case the presence of available free volume does not determine any change in the gel-arrested state ((B) and (C) panels), due to the fact that water cannot break clay bonds. The different behavior between the high and low concentration samples ((C) and (F) panels) observed in the dilution experiment confirms the different nature of the corresponding arrested states: a Wigner glass ($\mathbf{G_2}$) and a gel ($\mathbf{G_1}$), dominated respectively by repulsive and attractive interactions at high and low concentrations.

The striking result of a low-concentration gel network and of a high-concentration disconnected Wigner glass is at odds with previous studies of simpler systems [7, 8, 28]. We attribute this unexpected scenario to the separate timescales controlling the interactions and the two arrest processes [15]. While repulsion is felt almost immediately after samples are prepared, attraction, due to its anisotropic nature and to the presence of an effective repulsive barrier, develops on a much longer timescale as in reaction-limited aggregation. Long-time attraction may also affect the repulsive Wigner glass, through the formation of subsequent additional bonds. Indeed, rheological measurements for rejuvenated samples show a dependence on the idle time waited after the glass is formed [29]. To elucidate this point we have performed an additional dilution experiment on the high concentration sample waiting one week after dynamical arrest takes place. In this case the system does not melt, probably due to intervening long-time attraction which strengthens the glass. However the unmelted final state is different from that observed at low concentration, while the latter remains unchanged and water does not penetrate into it, the former seems to slowly absorb water in the bulk. SAXS measurements show that $S(Q)$ does not change significantly in this time window demonstrating that the disconnected structure of the repulsive glass is preserved despite the intervening attraction, and hence the resulting state cannot be considered an attractive glass in the most common sense.

In conclusion, through the combination of dilution experiments, SAXS experiments, theory and simulations, we have shown the presence of a disconnected Wigner glass state in a screened charged colloidal system. This arises at a larger (but still very low) concentration with respect to the one where a gel network is found, thanks to the different timescales controlling the repulsive (short-time) and attractive (long-time) interactions. We expect these findings to be relevant to other complex liquids with competing interactions as anisotropic patchy colloids [30] and globular proteins [31].

[1] P. N. Pusey and W. van Megen, Nature **320**, 340 (1986).
[2] F. Sciortino, Nat. Mat. **1**, 145 (2002).
[3] E. Zaccarelli, J. Phys. Cond. Matt. **19**, 323101 (2007).
[4] J. Groenewold and W. K. Kegel J. Phys. Chem. B **105** 11702 (2003).
[5] F. Sciortino *et al.*, Phys. Rev. Lett. **93**, 055701 (2004).
[6] H.M. Lindsay and P.M. Chaikin, J. Chem. Phys. **76**, 3774 (1982).
[7] J. C. F. Toledano, F. Sciortino, and E. Zaccarelli, Soft Matter **5**, 2390 (2009).
[8] P. Royall, H. Tanaka, submitted to Phys. Rev. Lett. (2009).
[9] A. Shalkevich *et al.*, Langmuir **23**, 3570 (2007).
[10] M. C. D. Mourad *et al.*, J. Phys. Chem. B **113**, 11604 (2009).
[11] http:www.laponite.com.
[12] A. Mourchid *et al.*, Langmuir **14**, 4718 (1998).
[13] D. Bonn *et al.*, Europhys. Lett. **45**, 52 (1998).
[14] P. Mongondry, J.F. Tassin, and T. Nicolai, J. Colloid Interface Sci. **283**, 397 (2005).
[15] B. Ruzicka, L. Zulian, and G. Ruocco, Phys. Rev. Lett. **93**, 258301 (2004); Langmuir **22**, 1106 (2006).
[16] F. Schosseler *et al.*, Phys. Rev. E **73**, 021401 (2006).
[17] S. Jabbari-Farouji *et al.*, Physical Review E **78**, 061405 (2008).
[18] B. Ruzicka *et al.*, Phys. Rev. E **77**, 020402(R) (2008).
[19] E. Trizac, *et al.*, J. Phys.: Condens. Matter **14**, 9339 (2002).
[20] S. Mossa, C. De Michele, and F. Sciortino, J. Chem. Phys. **126**, 14905 (2007).
[21] H. Z. Cummins, J. Non Cryst. Sol. **353**, 3892 (2007).
[22] T. Narayanan *et al.*, Phys. Rev. Lett. **96**, 258301 (2006).
[23] C. N. Likos Physics Reports **348**, 267 (2001).
[24] Hansen, J.-P.; MacDonald, I. R. *Theory of Simple Liquids*, Academic: London, 3rd edition, 2006.
[25] E. Balnois, S. Durand-Vidal, and P. Levitz, Langmuir **19**, 6633 (2003).
[26] F. Cardinaux *et al.*, Europhys. Lett. **77**, 48004 (2007).
[27] S. Kutter *et al.*, J. Chem. Phys. **112**, 311 (2000).
[28] A.I. Campbell *et al.*, Phys. Rev. Lett. **94**, 208301 (2005).
[29] A. Shanin and Y. Joshi, submitted to Langmuir (2009).
[30] S. C. Glotzer and M. J. Solomon, Nat. Mat. **8**, 557 (2007).
[31] R. Piazza, Curr. Op. Coll. Interf. Sci. **5**, 38 (2000)